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# X. *On the Properties of Voltaic Circles, in which concentrated Sulphuric Acid is the Liquid Conductor.* *By* THOMAS ANDREWS, M.D., *Professor of Chemistry in the Royal Belfast Institution.*

Read 9th April, 1838.

THE remarkable discovery of Professor Schœnbein of Bâle respecting the modification which the chemical action of nitric acid upon iron undergoes when they are brought into contact under certain voltaic conditions, has led me to examine the general phenomena which are exhibited by voltaic circles whose liquid conductor consists of a concentrated acid. In a paper read at the last meeting of the British Association, I showed that the solution of the oxidable metals in strong nitric acid is greatly retarded when they are voltaically associated with such metals as platina, upon which that acid has no action; a result which is evidently the reverse of the ordinary effect of the passage of an electrical current. The object of the present communication is to extend the same principle to the action of concentrated sulphuric acid under similar conditions, and to investigate some of the circumstances which influence the development of electrical currents in this way.

When a piece of zinc is introduced into strong sulphuric acid (sp. gr. 1.847) at common temperatures, its surface becomes covered with a mass of gaseous bubbles, so fine that they might be almost mistaken for a white precipitate, which very slowly separate from the zinc, but by agitation, or the application of a gentle heat, may be easily removed. The gas thus disengaged is hydrogen in a state of perfect purity. On applying heat to the acid there is scarcely any further extrication of gas, till the temperature has reached nearly 100° cent., when a very fine stream of gas begins to arise from the surface of the zinc. As the heat is raised, the quantity of gas becomes more considerable; from 120° to 150° cent. there is a rapid effervescence, and at still higher temperatures vast quantities of gas, mixed with the vapours of sulphur, are disengaged. On examination, this gas was found to consist of a mixture of sulphurous acid and hydrogen gas. When an excess of zinc was employed the hydrogen in the beginning of the process amounted to 20 per cent. of the whole, but towards the end it increased to nearly 40 per cent.

A similar portion of zinc being connected with a platina wire, and the free extremities of each being introduced into the same acid, so as to form a voltaic circle, the fine bubbles before described now appeared chiefly on the surface of the platina. When removed they did not form again, unless a fresh surface of zinc was exposed. The gas thus obtained was found to be pure hydrogen. The acid was then heated, but there was no extrication of gas from the surface of either metal till the temperature reached 150° cent., and then only a few minute streams arose from the platina wire. At 190° the evolution of gas from the platina wire did not exceed that from the unconnected zinc at 140° or 150°. From 210° to 240° there was rapid effervescence. During the course of the experiment no gas appeared at the surface of the zinc, unless the temperature was very high, so that torrents of gas were disengaged from the platina, when by a close inspection some very fine streams might be perceived forcing a passage from certain points of the zinc surface. The gas extricated from the surface of the platina differed from that obtained when the zinc alone was dissolved,—in the small quantity of hydrogen which it contained, and in that quantity diminishing instead of increasing as the solution proceeded. In fact the hydrogen was found to amount to 9 per cent. in the commencement of the experiment, and towards the end it diminished to only 1 per cent., the rest of the gas being sulphurous acid. A quantity of sulphur was also separated, both when the zinc was alone and connected with the platina, which sometimes appeared in crystals in the acid, at other times became diffused through the mass of the liquid, so as to render it nearly opake, while at high temperatures it was disengaged in the state of vapour.

Gold and palladium act in the same manner as platina.

There was no apparent difference in these results, whether pure zinc, or the sheet zinc of commerce was used, and from the uniform surface which it exposes, the latter was employed in all the following experiments.

To ascertain with precision the retarding influence of the platina upon the solution of zinc, similar portions of connected and unconnected zinc were exposed to the action of sulphuric acid of sp. gr. 1.845 at the same time and in the same vessel. The platina was placed opposite to both surfaces of the zinc, and at the distance of one-fourth of an inch; it exposed to the liquid a surface which was about one-third of that of the zinc. The connexion was made above the liquid. The following table contains the results of a series of experiments made at different temperatures, in which the second column gives the ratio of the quantities of zinc dissolved from equal weights of that metal, when alone and when united to platina, assuming as unit the quantity dissolved in the latter case.

| No. of Experiment. | Ratio of Zinc dissolved. | | | Temperature. |
|---|---|---|---|---|
| | Connected. | | Alone. | |
| 1 | 1 | : | 2.065 | 168° to 170° cent. |
| 2 | 1 | : | 2.255 | 203° to 206° „ |
| 3 | 1 | : | 2.347 | 221° to 233° „ |
| 4 | 1 | : | 3.000 | 238° to 240° „ |
| 5 | 1 | : | 3.208 | 242° „ |
| 6 | 1 | : | 1.478 | 250° to 270° „ |
| 7 | 1 | : | 1.335 | 265° „ |

Although the zinc was removed from the acid, and its loss ascertained, before its surface had undergone much alteration, yet as the connected zinc diminished less during the process of solution than the other, the surfaces became no longer precisely similar; and hence the differences exhibited by the table are less than they ought to be. From an inspection of the table, it appears that the greatest difference in the quantity of zinc dissolved occurs at the temperature of 242°, where the action of the acid is reduced to less than one-third by the contact of the platina; while at higher and lower temperatures the difference is less considerable. This circumstance may, perhaps, be explained by the following considerations. The rapidity of the solution of zinc, whether alone or connected, increases at a much faster ratio than the temperature, till it reaches a maximum point, when it can scarcely be augmented by farther increments of temperature. Now the effect of the contact of platina being to reduce the rate of solution of the zinc in the acid at a given temperature, (to what it is at 40° or 50° cent. lower than when unconnected,) it is evident that the difference will increase till they both attain such a temperature that they dissolve with the greatest possible rapidity when the difference will undergo a diminution.

The effect of the distance of the platina and zinc plates from each other in the acid was next investigated.

Two couples of platina and zinc, similar in every respect, except that in the one, the zinc plate and platina were in contact, and in the other, at the distance of .1 inch, were introduced into sulphuric acid, at the temperature of 225° cent. The quantity of zinc dissolved in the first couple was to that dissolved in the second as 1.587 : 1. When the distances between the platina and zinc were .1 and .5 inch respectively, the quantities of zinc dissolved were as 1.441 : 1. The temperature in this case was 230°. The galvanometer needle was also more strongly deflected when the metals were near each other. The action of the acid on the zinc therefore increases with the proximity of the platina, as in common voltaic circles. This is further shown by the parts of the surface of the zinc which are nearest the platina dissolving most rapidly.

Next the distance between the platina and zinc plates being the same, the extent of the platina surface in each couple was varied. The results obtained are exhibited in the following table, in which the second column shows the distance between the platina and zinc in the acid; the third, the extent of the platina surface in each couple referred to that of the zinc as unit; the fourth, the ratio of the platina surfaces to each other; the fifth, the ratio of the quantities of zinc dissolved with the respective platina surfaces; and the sixth, the temperature.

| No. of Experiment. | Distance between Plat. and Zinc. | Plat. surface, Zinc = 1. | Ratio of Plat. sur. | Ratio of Zinc dissolved. | Temperature. |
|---|---|---|---|---|---|
| 1 | $\frac{1}{8}$ inch. | 2.3 : 3.4 | 1 : 1.5 | 1 : .878 | 225° c. |
| 2 | $\frac{1}{8}$ " | 4 : 12 | 1 : 3 | 1 : .890 | 230° |
| 3 | $\frac{1}{8}$ " | .1 : .4 | 1 : 4 | 1 : .872 | 225° |
| 4 | $\frac{1}{9}$ inch. | .1 : .7 | 1 : 7 | 1 : .920 | 220° |
| 5 | $\frac{3}{5}$ " | .13 : 2 | 1 : 15 | 1 : .822 | 205° |
| 6 | $\frac{3}{10}$ " | 1 : 9 | 1 : 9 | 1 : .857 | 180° |

Although the variations in the extent of the platina surfaces, both when compared to each other and to the surface of the zinc, are very considerable, yet the quantities of zinc dissolved present only slight differences, and do not appear to be influenced by those changes in the platina surfaces. It must, however, be particularly observed, that there is invariably less zinc dissolved with the larger platina plate,—a result altogether at variance with the established laws of voltaic action.

To ascertain whether this apparent anomaly depended upon some peculiarity in the mode of generation of these currents, or on the ordinary action of the acid on the zinc being more completely checked by the broader platina surface, it appeared to be necessary to determine the quantity of electricity actually developed under these conditions. For this purpose a galvanometer, composed of a pair of astatic needles, with a single silver wire between them, was interposed in the course of the circuit. As the needle of such an instrument can scarcely be maintained in a stationary position, but oscillates through an arc of two or three degrees round a fixed point, the most accurate method of ascertaining its deflection is to make five or more observations of the extremities of the arcs through which it vibrates, and to take a mean of the whole; and this was the method followed in obtaining the deflections contained in the next table. As each degree of the scale occupied only one-fortieth of an inch, and was not subdivided into smaller parts, it was difficult to avoid an error of a quarter of a degree in making the observations. The second column of the annexed table gives the extent of the surface of the platina exposed to the liquid, that of the zinc being represented by 1; and the third column, the deflection of the needle of the galvanometer. The temperature was 156° c. during the whole course of the experiment, and the distance between the zinc and platina surfaces was one inch and a half.

| No. of Experiment. | Platina Surface, Zinc being = 1. | Deflection. |
|---|---|---|
| 1 | .8 | 30°.1 |
| 2 | .2 | 29°.8 |
| 3 | .08 | 30°.1 |
| 4 | .02 | 29°.9 |
| 5 | .01 | 27°.4 |
| 6 | .008 | 26° |
| 7 | .0008 | 14°.2 |

The trifling differences in the deflections of the needle, in the first four experiments, certainly depended upon the unavoidable errors of observation and minute variations in the temperature of the acid. The current was therefore not perceptibly affected by altering the extent of the platina surface exposed to the liquid, unless that surface was reduced to less than $\frac{1}{50}$ of the surface of the zinc; and even when it amounted to $\frac{1}{1250}$ of the latter, the deflection of the needle was only one-half less than with equal surfaces. This is very different from the well-known effect of similar changes in the extent of the surface exposed by the electro-negative metal in voltaic circles formed with the dilute acids. As a term of comparison, the platina surfaces used in experiments 1 and 4, being connected with similar zinc plates as before, and introduced into a mixture of dilute nitric and sulphuric acids, the deflections were 25°.5 and 7° respectively.

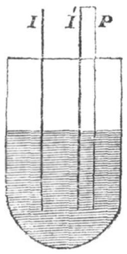
Although there was no visible disengagement of sulphurous acid gas from the zinc in the preceding experiments, except in No. 7, yet by comparing these results with those before obtained, it will appear that increasing the platina surface tends to arrest more completely the ordinary or local action of the acid on the zinc.

When a slip of zinc in heated sulphuric acid was made the positive pole of a galvanic battery of twenty pairs of plates in moderate action, sulphurous acid ceased to be evolved from its surface, and the solution of the metal was greatly retarded.

As a contrast with the preceding results, the influence of mercury, in connexion with zinc, upon the solution of the latter metal, may be mentioned. If these metals are heated separately in concentrated sulphuric acid, till a gentle effervescence occurs at the surface of both, and then brought into contact, a very violent chemical reaction instantly occurs, an amalgam appears at first to be formed, and afterwards the zinc dissolves with the utmost degree of violence. It is the most remarkable example of increased chemical action from the formation of a voltaic combination with which I am acquainted. These facts are the more singular, as it thus appears that the influence both of amalgamation and of contact with platina on the solution of zinc is reversed in dilute and concentrated sulphuric acid.

The general phenomena presented by the other metals capable of decomposing sulphuric acid were similar to these already described in the case of zinc, but in the details there were some important points of difference.

Two similar *iron* wires, I and I′, were placed in a glass tube containing concentrated sulphuric acid, I being alone, and I′ connected with a platina wire finer than itself. When first immersed in the acid the fine bubbles before described appeared at P and I, none at I′. On heating the liquid vast volumes of gas were extricated from I, but there was no gas visible at P or I′ till the liquid was raised nearly to the point of ebullition, when there was some effervescence at P, and slight local disengagement of gas at I′.



When pencils of *tin*, T and T′, (T being unconnected, and T′ connected with the platina P, and similar designations are used for the following metals,) were substituted for the iron wire; the same phenomena occurred in the cold acid as with zinc and iron. Heat being applied to the acid, gas appeared at the same time at T and P; but on raising the temperature a little higher, the action suddenly became so violent on T that it was impossible to observe the surfaces of T′ and P. By heating T′ and P in a separate tube, the quantity of gas at P became very considerable, but far less than that before given off from T. There was also an obvious extrication of gas from T′.

With *bismuth* no gas appeared in the cold. On applying heat the surface of B became covered with a dark film, and soon afterwards that of B′. Continuing to apply the heat, gas was disengaged from P and B, but in much greater quantity from the latter. There was very little gas from B′.

*Antimony* gave precisely similar results to bismuth, except that there was rather more gas extricated from the metal connected with the platina when the temperature was high.

With *silver* no gas appeared in the cold. On applying heat S and S′ became dark nearly at the same moment; as the heat was raised, gas was abundantly disengaged from S, and in smaller quantities from S′ and P, but in the case of this metal the quantities of gas extricated from S′ and P appeared to be equal.

With *arsenic* and *mercury* there was no action in the cold. When the acid was heated the disengagement of sulphurous acid appeared to be scarcely, if at all, diminished, by connecting these metals with platina. The quantity of gas also extricated at the surface of the platina was very trifling.

Taking a general view of these results, it will be observed, that the evolution of hydrogen gas, on immersion in the cold acid, occurred only with the metals, zinc, iron, and tin. The phenomena exhibited in this case by the platina and zinc couple afford a remarkable example of the cessation of a chemical action from the surface of the zinc acquiring a peculiar or polarized state. For although a large mass of bubbles appeared at first, yet by heating gently the liquid these not only were separated, but not the least trace of gas afterwards appeared at either surface. There is a striking analogy in this, to the action of nitric acid of certain strengths upon some of the metals.

In the cases of iron and zinc, the disengagement of gas was wholly transferred from the surface of these metals to that of the platina in connexion with them; in those of bismuth, antimony, and tin, there was slight extrication of gas at the surface of the dissolving metal; in that of silver, the quantity of gas was nearly the same from the platina and silver; while in the cases of arsenic and mercury, scarcely any gas was given off from the platina, the action of the acid on the two latter metals not being perceptibly diminished by contact with platina.

If these results are compared with those which have been already obtained with nitric acid, it will be evident that in the case of the concentrated acids the formation of a voltaic circle has in general the tendency to diminish chemical action. The following law will be found to be generally, although not universally true, the exceptions to it being probably, however, rather apparent than real.

*The ordinary chemical action of an oxy-acid upon the metals soluble in it, is, in general, diminished when the acid is concentrated, by voltaically associating them with certain electro-positive metals; but on the contrary, is increased when the acid is dilute.*

In the preceding experiments the diminution of chemical action occurred in cases in which the acid itself suffered decomposition; while in common voltaic circles, where it is well known that the action is increased, the elements of water alone are eliminated; but how far this coincidence may be universal, must be determined by future investigations.